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Miscible blends of poly(benzoyl paraphenylene) and polycarbonate

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Abstract

Substituted poly(paraphenylene) derivatives (PX) have recently gained interest due to their unique properties [1–5]. They are amorphous thermoplastics with relatively modest glass transition temperatures ($T_g \sim 150$°C), are soluble in various common organic solvents, and yet possess the strongest mechanical properties of any amorphous thermoplastic [6]. However, the blend behavior of these polymers is relatively unexplored. Here we report the phase behavior of PX and various thermoplastic blends and highlight the PX and polycarbonate (PC) blends which were found to possess a lower critical solution temperature (LCST) as determined through enthalpy relaxation and cloud point measurements. The morphology and storage moduli of the PX/PC blends have been observed in both the single phase and two phase regimes.
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Keywords: Poly(benzoyl paraphenylene)/polycarbonate blends; Phase behavior; Miscible

1. Introduction

Studies of engineering thermoplastics have revealed that compositions having a large fraction of aromatic groups along the backbone tend to exhibit increased temperature stability and improved mechanical properties. One such highly aromatic backbone structure is poly(paraphenylene) (PX). Previous attempts at synthesizing high molecular weight rigid-rod poly(paraphenylene) polymers have met with limited success because the materials were insoluble in solvents and infusible [3]. Recent studies have shown that with short side-chains on the backbone, solubility is increased and a high-molecular-weight, high-intrinsic-viscosity polymer can be obtained [7,8]. Thus in the resulting PX polymer (Fig. 1), the backbone still serves to strengthen and stiffen while the side-chains afford solubility in many common organic solvents. This combination leads to unique characteristics for the polymer and has led to the terms 'thorny-rods' [5] and 'self-reinforcing polymers' [6] to describe these materials.

PX polymers thus far have not exhibited any signs of crystallinity or liquid crystallinity despite their rigid nature. This is attributed to the side-chains which break up the tendency for close, orderly packing. The increased free volume due to the side-chains may also account for their relatively modest T_g of approximately 150°C. The backbone serves to give PX a low dielectric constant (~3.2 at 1 MHz) as well as good flame resistance [9]. Furthermore, PX can retain almost all of its weight even at 500°C in air [9]. Additionally, the highly conjugated backbone gives PX not only the highest tensile modulus (~10 GPa) of known thermoplastics but also excellent tensile and compressive yield strength (~200 MPa) [10]. All of these properties point to a material which is suitable as a replacement material for numerous structural applications. Unfortunately, PX's use has been limited due to its high melt viscosity, which poses considerable difficulty in traditional polymer processing operations.

One potential method of overcoming this difficulty is blending PX with other thermoplastics. However, only a few blend phase behavior studies have been performed thus far [6], and as can be expected, most blends are immiscible. Interestingly however, is the fact that certain blends of PX with polyimides, polysulfones, and polycarbonate (PC) are known to give transparent films when solvent-cast [6]. Optically clear blends may be of significant commercial importance. In addition, optical clarity of blends suggests further investigation to determine whether the blends are thermodynamically miscible. In the case of PX blends in particular, miscibility may be useful for improving processability while retaining most of the advantageous mechanical properties.

We report here the phase behavior of several PX/thermoplastic blends. The PX/PC blend phase behavior has been studied in detail utilizing enthalpy relaxation and cloud

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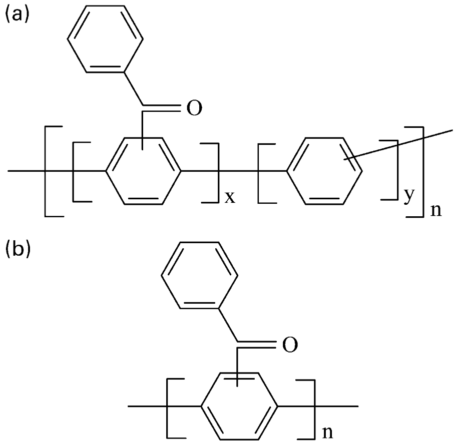

Fig. 1. The chemical structure of (a) PX1200 and (b) PX1000. The PX1000 has 100% para-linkages while the PX1200 contains approximately 15% meta-linkages which do not contain any side-chains.

point measurements to demonstrate an LCST behavior. The morphology of the PX/PC blends is also determined with scanning electron microscopy (SEM). Additionally, the storage moduli of the blends have been measured.

2. Experimental

2.1. Materials

Two variations of the benzoyl substituted Parmax™ resins were supplied by Maxdem Inc. The PX1000 grade contains 100% para-linkages along the backbone while the PX1200 is a copolymer with approximately 85/15 (mol/mol%) benzoyl-1,4-phenylene (Fig. 1). The relative amounts of the meta and para-linkages from the phenylene units are not precisely known. The weight-average molecular weight (M_w) of the PX1200 has been reported as 26,900 g/mol as determined by light scattering [1], and the PX1000 has been reported to have a number-average molecular weight (M_n) of about 17,000 [2]. The polydispersity index for both pairs is 2.3 as measured by gel permeation chromatography (GPC). Note that the PX1000 has a M_n of 17,000 and PX1200 has a M_n of 11,700.

The Lexan 101 polycarbonate (PC), supplied by General Electric, has a M_n of 21,000 with a polydispersity index (PDI) of 1.7, as determined by GPC, which was calibrated using a polystyrene standard running with THF at 30°C. Ultem 1000 polyetherimide (PEI), with a reported M_n of 20,000 [11], was also supplied by General Electric. The poly(methyl methacrylate) (PMMA) used was AtoHaas grade VO45 with a melt flow index of 2.3 (230°C/3.8 kg). The Eastar 6763 poly(ethylene-co-cyclohexane dimethylene terephthalate) (PETG) supplied by Eastman Chemical Company had a M_n of 26,000. Polystyrene (PS) PS 1424 was supplied from BASF, which has a melt flow index of 2.5 (200°C/5.0 kg).

2.2. Sample preparation

The as-supplied PX powders were dissolved in dichloromethane at a 10% (weight/weight%) concentration at room temperature and precipitated into methanol to ensure purity of the resins. The resulting polymer was then dried in a vacuum oven heated to 70°C overnight to remove final traces of any solvent. The as-received PC pellet and precipitated PX of appropriate weight fractions were then dissolved in dichloromethane. The PC solutions were clear and colorless while the PX solutions were clear but had a pale yellow color. The blends were also solution mixed in dichloromethane, and clear solutions were formed. The solutions were then cast in a petri dish with a cover to achieve a slow evaporation rate. PC crystallization could be inhibited through this method. The resulting films were clear, and these were again dried in a vacuum oven at 70°C for 24 h to remove any trace amounts of residual solvent. Other PX/thermoplastic blends were also prepared in equivalent manner.

It is important to note that care was taken to remove impurities from the PX samples which may not be the case in the commercial grade PX. Furthermore, the likelihood addition of processing aids to the PX in commercial situations may further complicate phase behavior.

2.3. Differential scanning calorimetry

For the samples which possess discernibly different T_g's, a Perkin-Elmer DSC7, calibrated with indium and zinc reference standards, was used at a heating rate of 20°C/min from room temperature to $T_g + 50$°C (of the higher T_g component). After 1 min of annealing, the samples were then quenched, at a rate of 100°C/min, back to room temperature and the second heating curve was used to determine the T_g.

2.4. Enthalpy relaxation measurements

To test for miscibility, approximately 7 mg samples of PX/PC blends of various compositions were placed in aluminum DSC pans and heated to 170°C, held at that temperature for 10 min, then quenched to 130°C and annealed for approximately 40 h to allow physical aging to take place. After aging, they were quenched at a rate of approximately 100°C/min to room temperature. The enthalpy relaxation was measured using the results of the first heating run, in which the materials were heated from 50 to 210°C at a rate of 20°C/min. To test for immiscibility, samples were held at 265°C for 15 min instead of at 170°C, with subsequent treatments the same.

2.5. Cloud point measurements

The system used by Bae et al. [12] has been adapted. A photodiode fitted on top of an optical microscope was used to measure the intensity of light passing through a polymer

Table 1
Glass transition temperatures of immiscible PX/thermoplastic blends (Error estimates are approximately ±2°C for all measurements)

Composition (PX/other)	PX/PEI		PX/PS		PX/PETG		PX/PMMA	
	T_{g1} (°C)	T_{g2} (°C)	T_{g1} (°C)	T_{g2} (°C)	T_{g1} (°C)	T_{g2} (°C)	T_{g1} (°C)	T_{g2} (°C)
0/100		220		102		81		96
20/80	157	219	156	101	156	81	156	95
40/60	157	218	156	103	156	81	157	96
60/40	156	216	156	102	156	80	156	97
80/20	156	213	156	103	155	81	156	95
100/0	155		156		156		155	

Table 2
Refractive index of the polymers as reported in product data sheets

	PX1000	PX1200	PC	PS	PMMA	PETG
Refractive index	1.71	1.66–1.70	1.59	1.57–1.60	1.49	1.57

film as a function of temperature. A 5°C/min scan was initially chosen to obtain an estimate of the phase separation temperature and a 1°C/min scan was subsequently run to precise the temperature. The output was recorded using a computer and the cloud point was determined by the first deviation from initial intensity in the log intensity vs log temperature curves.

2.6. Thermal expansion coefficient measurements

Approximately 2 mm thick samples were compression molded from the precipitated powders into 4×6 mm rectangles at temperatures approximately 100°C above the corresponding glass transition temperatures and cooled down to room temperature at approximately 1°C/min. The linear thermal expansion coefficient was then measured using Perkin-Elmer TMA7 at a heating rate of 1°C/min.

2.7. Scanning electron microscopy

Fracture surfaces prepared at room temperature or liquid nitrogen temperature did not exhibit sufficient contrast to determine the blend morphology. In order to achieve contrast, the samples were first embedded in epoxy and microtomed to obtain a flat surface. The PC component was preferentially etched by submersion for approximately 15–30 s in toluene, after which the etching was arrested by immersion into deionized water. Prior to examination, the samples were coated using a planetary gold coater and the images recorded with a Leo 438VP SEM operating at 20 kV.

2.8. Mechanical tests

The storage moduli were measured on a Seiko 200S DMTA operating at 1 Hz. The one phase blend samples were prepared by the solution casting method described earlier, and the two phase blends were prepared by annealing the single phase films at 265°C for 15 min. The films were cut into approximately 2 mm wide by 10 mm long samples ranging in thickness between 0.1 and 0.2 mm.

3. Results and discussion

The films obtained from solution cast blends of PMMA, PEI, PS, and PETG with PX were all optically opaque and the blends were found to be immiscible as determined from DSC measurements. The results are shown in Table 1 which demonstrates two separate T_g s in the case of each blend. It is interesting to note that Marrocco et al. [6] have reported PEI/PX blends cast from chloroform to form clear films (although shown by DSC to be biphasic), while our films cast from dichloromethane were opaque. DSC results suggest that the pair may be partially miscible as signified by the slight increase of both the T_g of PX and of PEI with increasing PEI content. The similarity of the T_g of PC to that of PX did not allow us to draw any conclusion concerning the miscibility of the blends using this method, and thus, enthalpy relaxation was employed. The method allows the determination of miscibility of blends that possess similar transition temperatures and has recently been review by ten Brinke [13]. Essentially its basis is the premise that most polymers will relax differently when aged even when they possess identical transition temperatures. Thus, if a binary blend is immiscible, two relaxation peaks, corresponding to the components' individual relaxation behavior, should appear when scanned after relaxation is allowed to occur. This is in contrast to a miscible blend which should only contain one relaxation peak throughout its composition range.

Fig. 2 shows the results for the enthalpy relaxation of PX/PC blends which were held at 170°C for 10 min and relaxed as described in the Experimental Section. The figure clearly shows only one relaxation peak for each composition which shifts to higher temperatures with increasing amounts of PX. We speculate that the miscibility arises from the favorable interaction between the $C=O$ polar groups. It is also interesting to note that the relaxation process does not take place linearly between the two outer limits, as has been observed in many other miscible blend systems [14]. We assume that this is either due to the rigid-rod nature of the PX, which does not allow relaxation to occur in a proportionate manner, or to the fact that with longer aging times, the PX chains become stiffer as has been reported by Dean et al. [2].

Cloud point measurements of PX1200/PC and PX1000/PC blends are shown in Fig. 3. A lower critical solution temperature (LCST) appears for both pairs—with the PX1000/PC blend possessing a lower demixing temperature relative to the PX1200/PC blend. While there is a higher number of carbonyl groups per repeat unit in PX1000, we believe that this favorable interaction is outweighed by the higher molecular weight of the PX1000.

As McMaster [15] has shown through Flory's modified equation-of-state model, an LCST behavior is expected for most miscible binary polymer pairs. The favorable enthalpic interaction between the two pairs is overcome with increased temperature and phase separation occurs due to the differences in the respective thermal expansion coefficients (α). McMaster showed that even a 10% difference in α with equivalent molecular weights led to an LCST behavior. The α values above the T_g of PC are calculated [16] and measured to be approximately 200 ppm/°C and PX1200 is measured to be approximately 470 ppm/°C. Note that PX1200 has one of the largest α of thermoplastics.

It is important to note that the presently determined phase diagram employed an experimental scanning rate of 1°C/min. While this is rather slow, phase separation times for high viscosity polymers can also be quite long. In order to unambiguously demonstrate thermodynamic miscibility, 40/60 PX1200/PC samples, which were first annealed at 265°C for 15 min to induce a two phase system (as characterized by opacity), were re-annealed at several lower temperatures in order to find the temperature at which the samples again became clear. Results have shown that at 190°C, samples became clear after 12 hours and reheating of these films up to 265°C once again induced phase separation. Thus, the thermodynamic nature of the PX-PC miscibility is clear, but the derived cloud point diagrams of course reflect a combination of thermodynamic and kinetic effects.

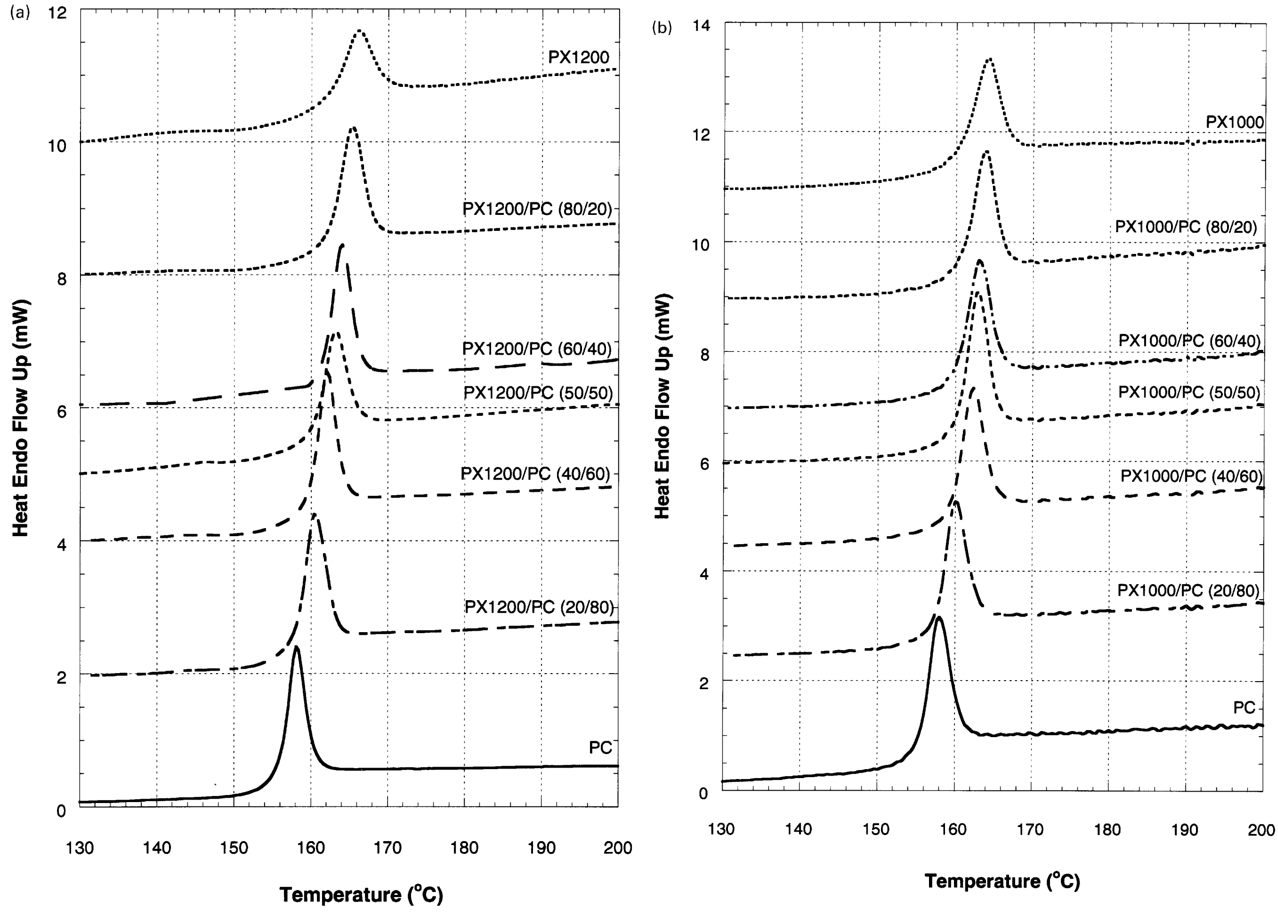

Fig. 2. Enthalpy relaxation curves of (a) PX1200/PC and (b) PX1000/PC blends that were heated to 170°C for 10 min, quenched to 130°C, and aged for 40 h. Single relaxation peaks are indicative of miscibility of the blends throughout the composition range studied.

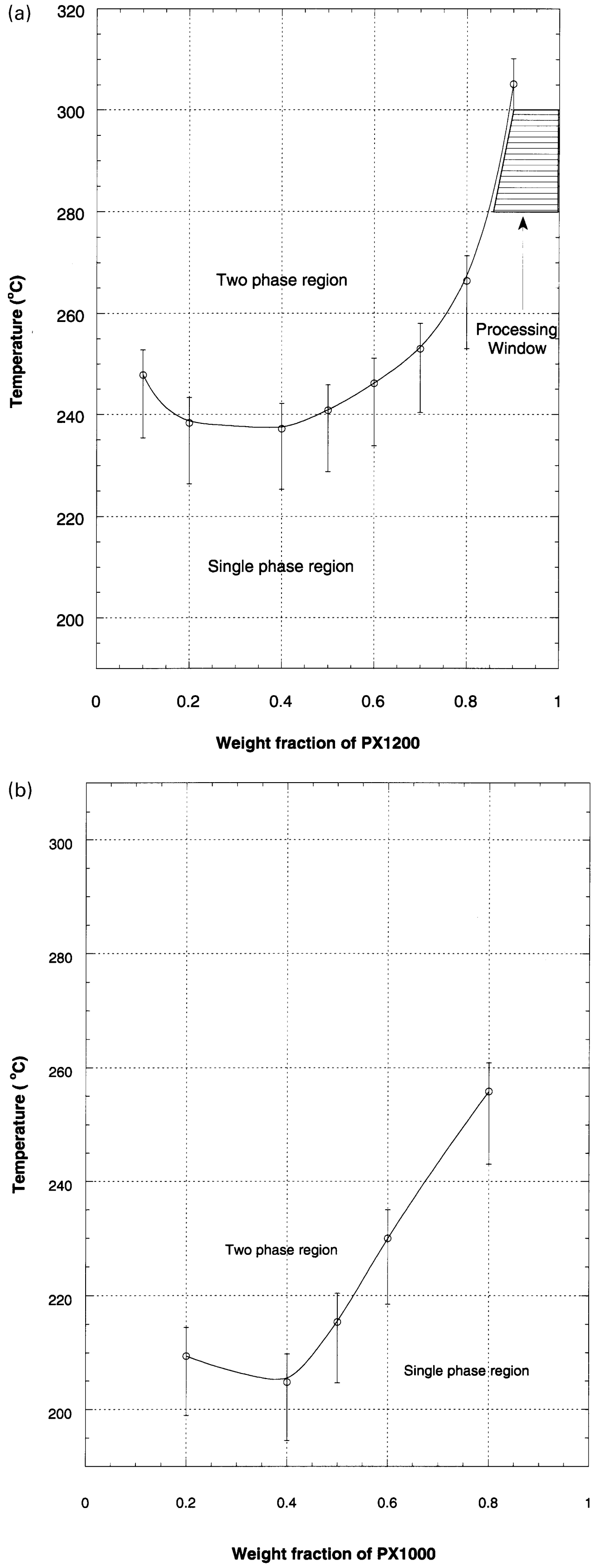

Fig. 3. The phase diagrams of (a) PX1200/PC blends and (b) PX1000/PC blends as obtained from cloud point measurements. The PX1200/PC blend possess a possible processing window at low concentrations of PC.

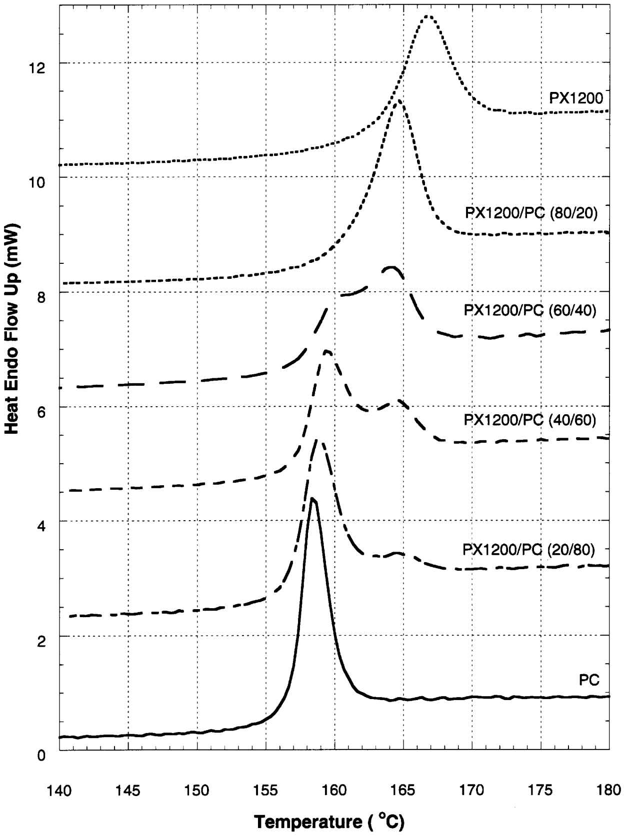

Fig. 4. Enthalpy relaxation curves of PX1200/PC blends that were heated to 265°C for 15 min, quenched to 130°C, and aged for 40 h. This verifies the cloud point data accuracy to ±3°C for samples held at 265°C for 15 min. The presence of two peaks indicates immiscibility.

Enthalpy relaxation experiments were also used to confirm the results of the cloud point measurements, as shown in Fig. 4. The samples of PX1200/PC were held at 265°C for 15 min, quenched to 130°C, and allowed to relax for approximately 50 h. The cloud point diagram predicts that only the greater than 80/20 PX1200/PC compositions will be single phase and indeed the results for a 15 min anneal confirm this fact.

The SEM images in Fig. 5 give visual confirmation of the blend behavior. Fig. 5(a) and (b) shows the microtomed and solvent etched surface of a pure PX1200 and a pure PC sample. Toluene has clearly left the surface of PX1200 undisturbed, while the pure PC surface has been aggressively dissolved away. For this reason, where PC is the matrix, the morphology is more difficult to observe than the PX-rich blends. Fig. 5(c)–(f) are micrographs of PX1200/PC blends which have been annealed at 265°C for 15 min. These micrographs clearly show the transition from the two phase blends with dispersed spherical PX particles embedded in a matrix of PC for the 20/80 PX1200/PC in Fig. 5(c) to that of a bicontinuous phase in the 60/40 PX1200/PC blends in Fig. 5(e). Furthermore, the 80/20 PX1200/PC exhibits no signs of multiple phases due to the fact that it is still kinetically trapped as a miscible

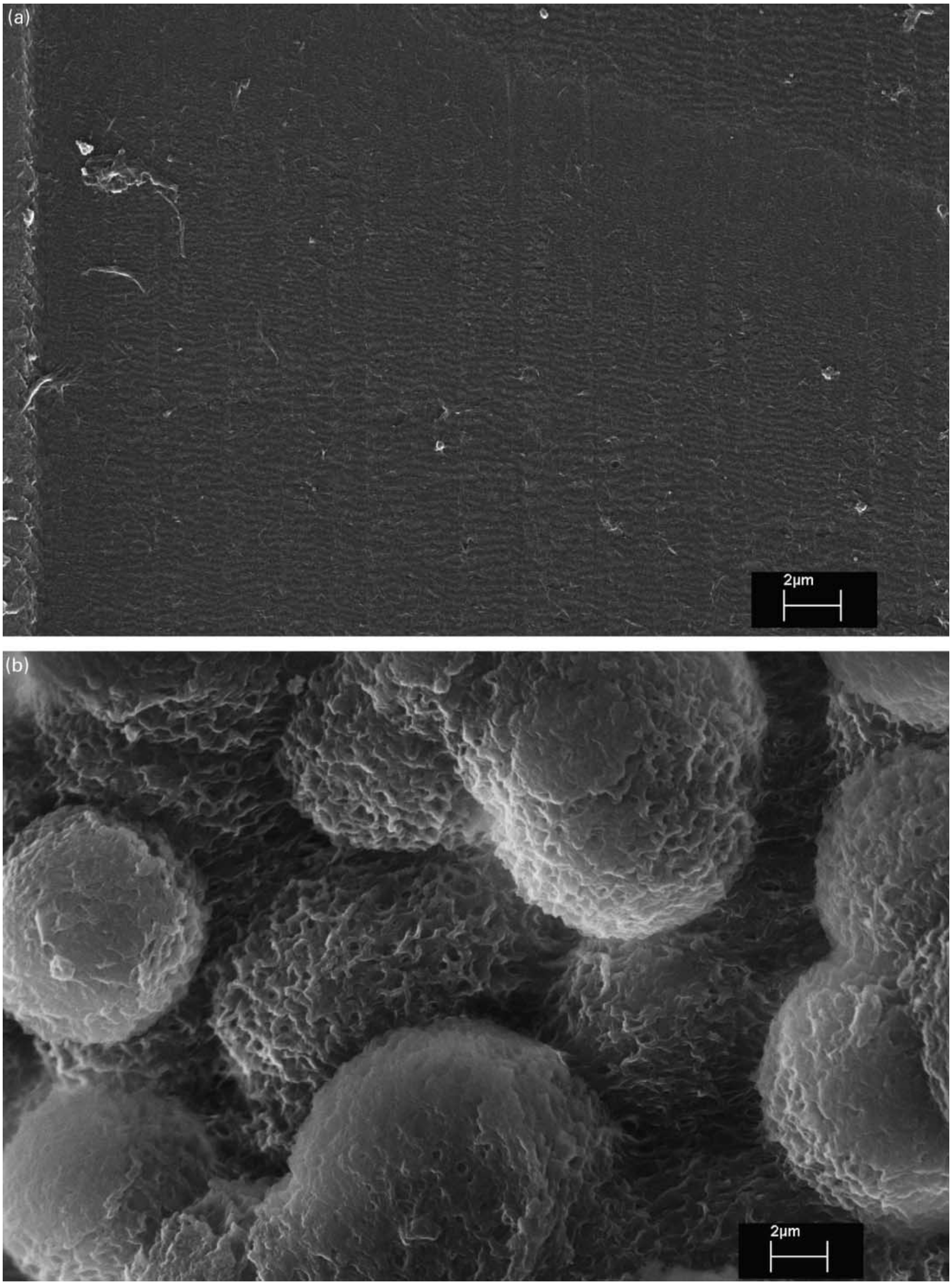

Fig. 5. (a) and (b) show the toluene-etched (~15 s) surfaces of the PX1200 and PC, respectively. PX1200 has not been affected while PC shows significant rearrangement. (c)–(f) show the toluene-etched (~15 s) surfaces of PX1200/PC blends from 20/80, 40/60, 60/40, and 80/20 after a 265°C anneal, respectively. (c)–(e) show the immiscible blend morphology while 5f) shows no dispersed phase. (g) shows the toluene-etched (~15 s) surfaces of solution cast PX1200/PC (80/20) blend. This is representative of other compositions.

blend since samples which were annealed for about 2 h begin to show faint signs of scattering. When compared to the sample which was not annealed (Fig. 5(g)), the similarity is very pronounced. SEM images of other compositions which have not been annealed are omitted, as Fig. 5(g) is representative of all the samples. Similar miscible to immiscible morphology transitions are observed for the PX1000/PC blends by SEM.

The storage moduli of the single phase and two phase PX1000/PC films have been measured to illustrate the effect of the morphology on the properties of the blends. It is expected that single phase blends will exhibit moduli

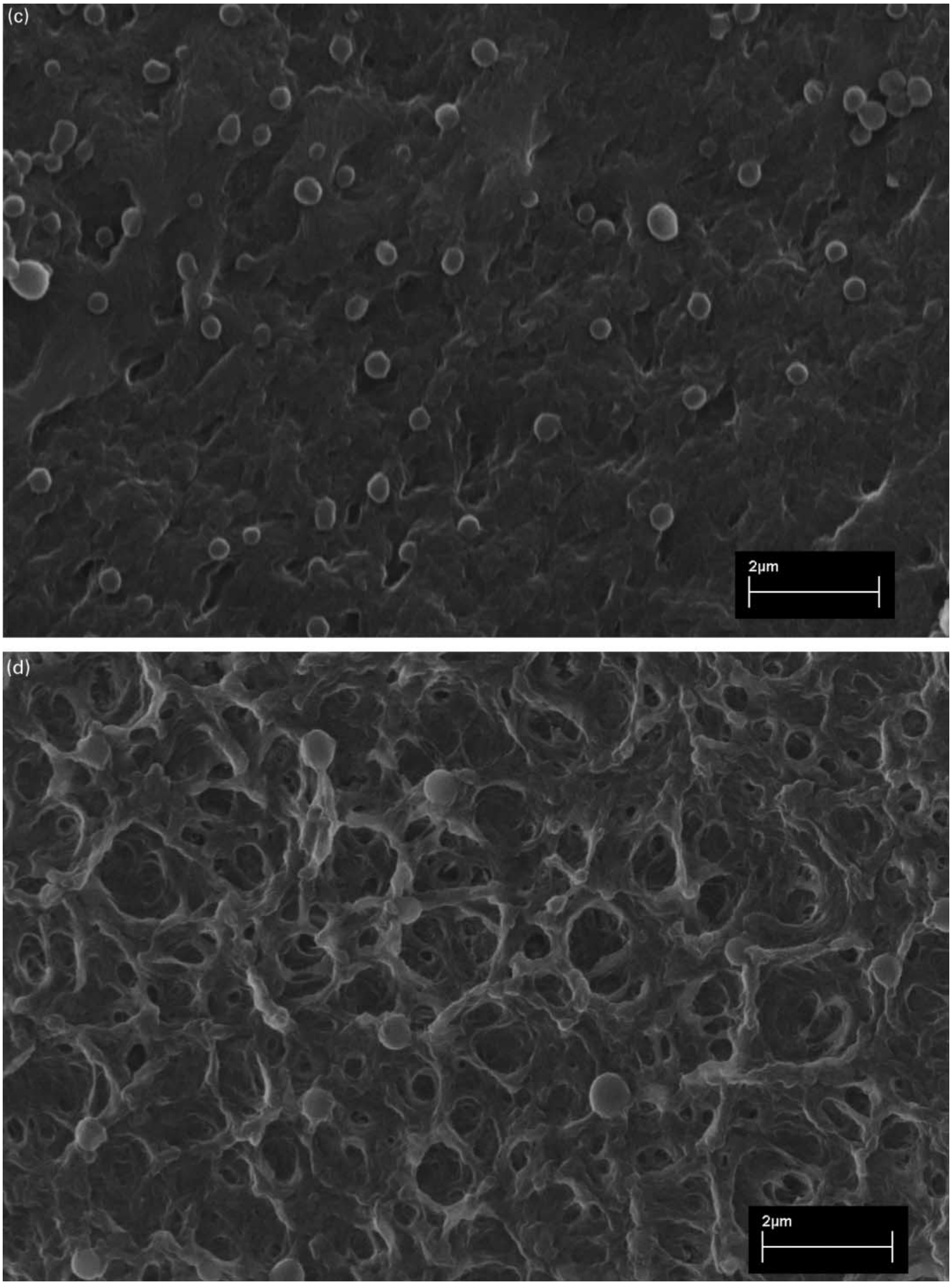

Fig. 5. (*continued*)

which are an average of the pure materials, weighted for their composition. The results shown in Fig. 6 confirm this prediction. The two phase blends exhibit lower moduli from those of the miscible blends as shown in Fig. 6. Many theories have been proposed in the literature, and the prediction of the blend behavior depends on many morphological details. The simple series model proposed by Takayanagi [17] seems to fit the data well.

Importantly, these results indicate a potential melt processing window for miscible PX1200/PC blends with PC concentrations up to about 15 wt%, as shown in Fig. 2(a), where miscibility can aid the difficult melt processing of the PX resins without significantly lowering the resultant mechanical properties. Furthermore, the enthalpy relaxation experiments seem to suggest that the processing window is accurate to about ±3°C if the operations were performed

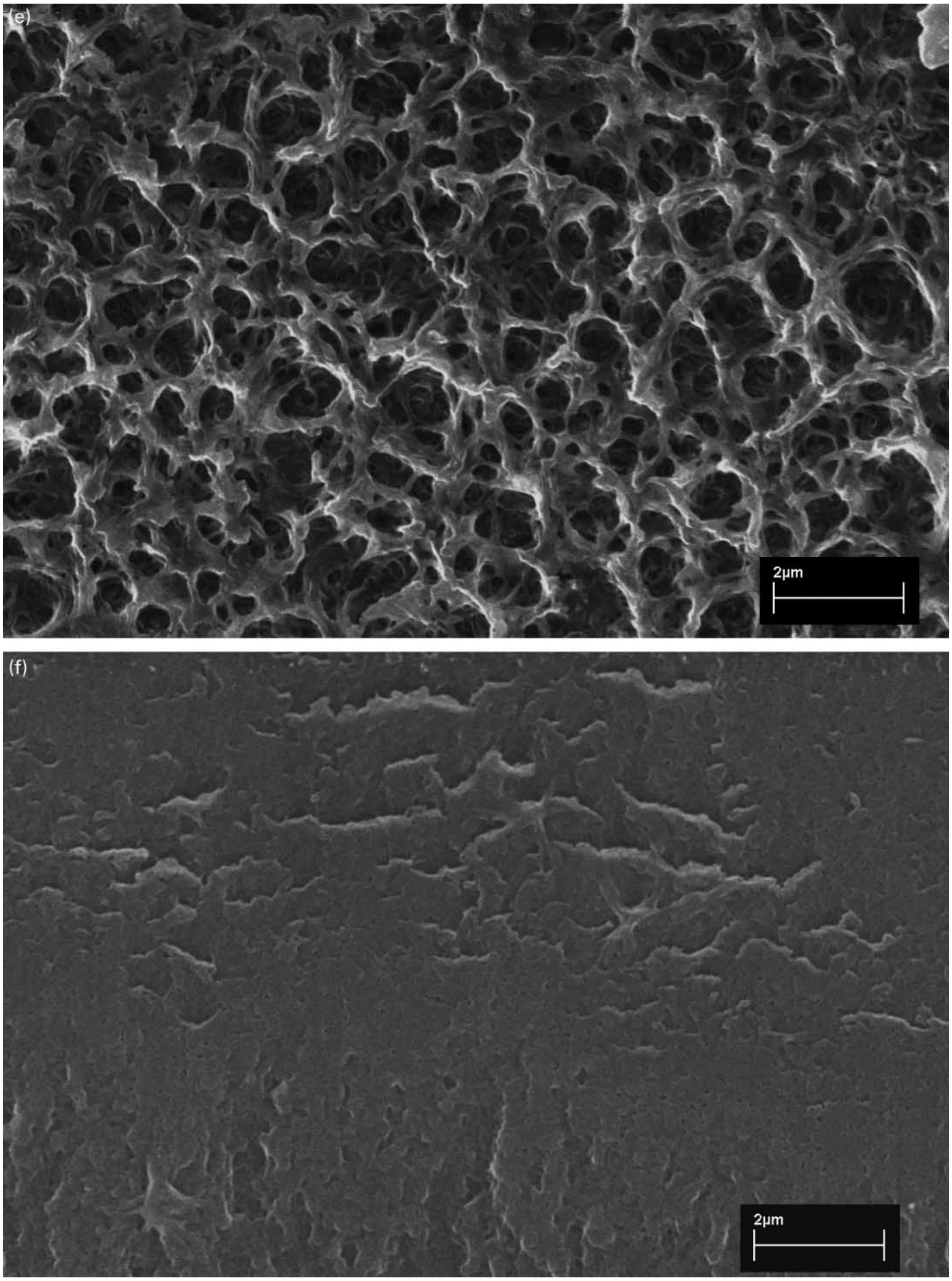

Fig. 5. (*continued*)

under 15 min. Unfortunately, it is unlikely that there is a similar processing window for PX1000/PC blends. In these blends, phase separation occurs at a lower temperature, making the single phase region substantially less accessible. Processing temperatures of at least 300°C are required for a melt viscosity of 10^5 poise at a shear rate of $10^2\ s^{-1}$ for the pure PX1200 materials. Temperatures of 350°C are required to achieve the same viscosity at the same shear rate for the PX1000 materials [18].

Despite the fact that PX is not a traditional 'rod' polymer, as a suggestion for future work, a study on the detailed conformation of PX [19] along with the detailed study of the influence of the paraphenylene content in PX1200 on the phase behavior may help to elucidate the necessary

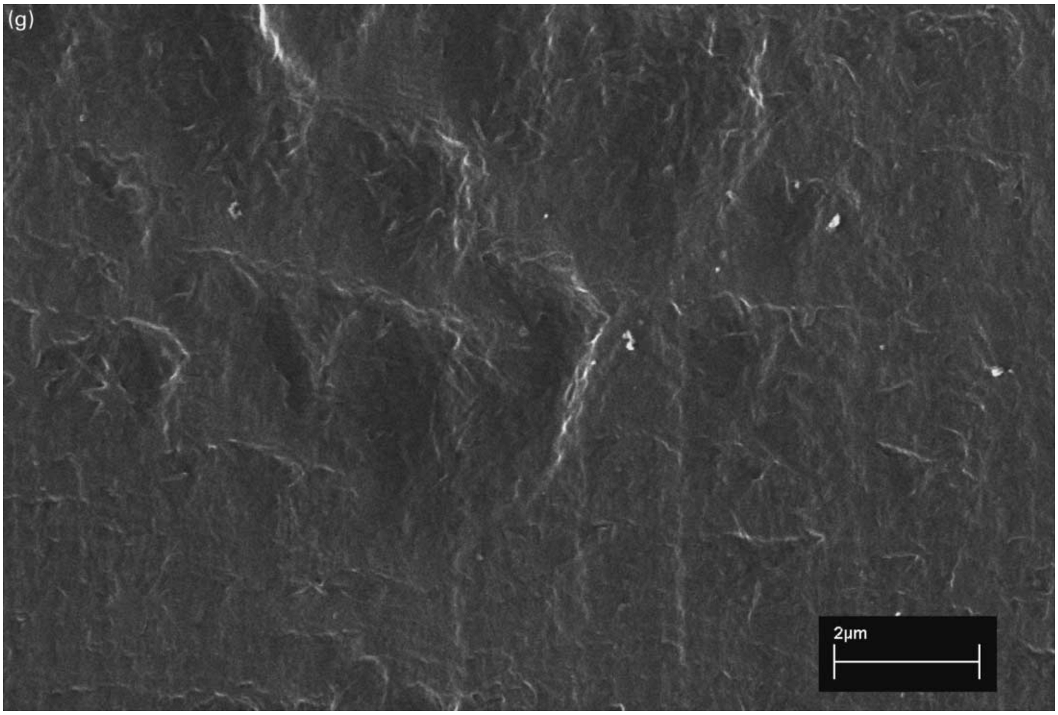

Fig. 5. (*continued*)

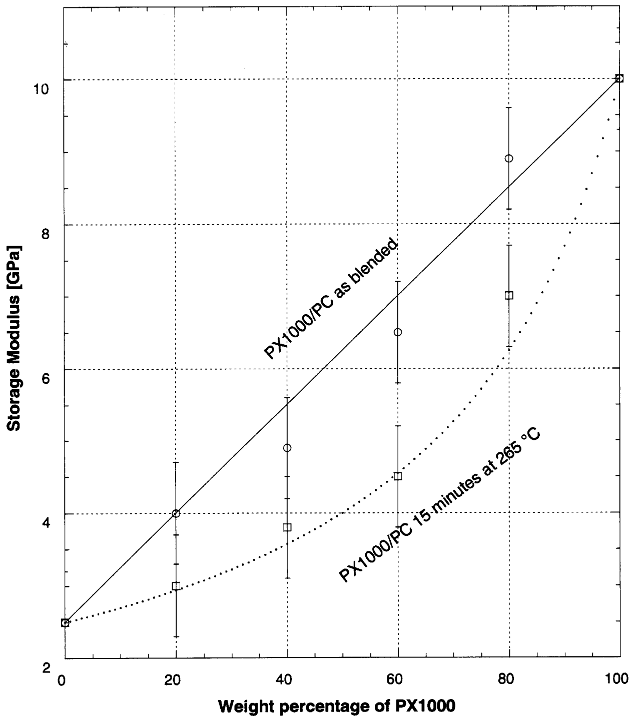

Fig. 6. Storage modulus of PX1000/PC blends which show a linear variation for the single phase blends as predicted. For the blends which have been annealed at 265°C for 15 min to produce phase separation, a series model deviation is followed, and results in lower values.

fundamental thermodynamic interactions in achieving ‘thorny’ rod-coil blends.

4. Conclusions

Blends of poly(benzoyl paraphenylene) with poly(methyl methacrylate), poly(ether imide), polystyrene, or poly(ethylene-co-cyclohexane dimethylene terephthalate) were found to be immiscible. However, PX1000/PC and PX1200/PC blends are miscible showing a LCST of 205 and 235°C, respectively, as verified by means of enthalpy relaxation, cloud point measurements, and SEM. Mechanical properties show that a miscible blend is more desirable than an immiscible one for higher-modulus applications. Our results indicate a potential processing window for optically clear PX1200/PC blends which may be able to improve ease of processing without significant reduction of mechanical properties.

Acknowledgements

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